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High-temperature Nanoindentation of Epitaxial ZrB₂ Thin Films

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Abstract

We use in-situ heated nanoindentation to investigate the high-temperature nanomechanical properties of epitaxial and textured ZrB₂ films deposited by magnetron sputtering. Epitaxial films deposited on 4H-SiC(0001) show a hardness decrease from 47 GPa at room temperature to 33 GPa at 600°C, while the reduced elastic modulus does not change significantly. High resolution electron microscopy (HRTEM) with selected area electron diffraction of the indented area in a 0001-textured film reveals a retained continuous ZrB₂ film and no sign of crystalline phase transformation, despite massive deformation of the Si substrate. HRTEM analysis supports the high elastic recovery of 96% in the films.

Keywords: sputtering; borides; ceramic thin film; nanoindentation; transmission electron microscopy

Zirconium diboride (ZrB₂) is a high-melting point ceramic that has been shown to exhibit high hardness and elastic modulus as well as good wear-corrosion resistance in the bulk form [1]. These properties are potentially useful for thin film applications, like cutting tools, aerospace, and electronics [2]. Thin film growth of ZrB₂ with well-defined properties is, however, complicated as the literature reports nonstoichiometric films or films with high amount of contaminants, especially oxygen. A promising advancement is our recent demonstration of epitaxial growth of stoichiometric ZrB₂ films by direct current magnetron sputtering (DCMS) using a ZrB₂ compound target [3] [4].

Few data on high-temperature hardness and Young's modulus of ZrB₂ have been published for bulk single-crystal and polycrystalline material. Nakano and Matsubara reported the Knoop hardness of single-crystal ZrB₂ [5]. They found that the hardness in each plane of the crystal decreases monotonously in the temperature range 300-

1100 °C from 27 to 9.8 GPa when the indentation is done on the {0001} plane, and from 20 to 6 GPa on the {10 $\bar{1}$ 0} plane. Xuan *et al* also studied the microhardness of single-crystals, but using a Vickers indenter with a load of 200 g [6]. The hardness is reported to decrease rapidly from 21.3 GPa at room temperature to 12 GPa at 400 °C, then the decrease slows down to 9 GPa at 700 °C, and finally reaches a constant value of 7.85 GPa at 1000 °C. Bsenko and Lundström studied the Vickers microhardness of polycrystals with an applied load of 50 g [7]. They reported a hardness decrease from 30 GPa to 8.5 GPa when the temperature is increased from 25 to 600 °C. Wang *et al* developed a cross-bar Vickers technique for determining the hardness of polycrystalline hot-pressed ZrB₂ at very high temperatures, up to 2000 °C [8]. Their experiments show that H decreases from 6.2 GPa at 1100 °C to 0.6 GPa at 2000 °C. Regarding Young's modulus, Okamoto *et al* found a monotonically decrease from 525 to 475 GPa when the temperature increases from 25 to 1100 °C on their polycrystalline material [9], while Wiley *et al*, measuring also polycrystalline ZrB₂ samples, reported a decrease from 493 to 448 GPa when the temperature increases from 25 °C to 1000 °C [10]. To our knowledge, no data is available about the high-temperature hardness and elastic modulus of ZrB₂ films.

In this work, we investigate the high temperature nanomechanical properties of epitaxial ZrB₂ films deposited by DC magnetron sputtering from a 3-inch circular target on 4H-SiC(0001), as well as weakly 10 $\bar{1}$ 0 textured ZrB₂ films grown on Si(100) held at floating potential using a deposition process described recently [3]. The deposition temperature and power discharge were 900 °C and 425 W for the film on SiC, and 850 °C and 400 W for the film on Si, respectively. For comparison, we investigated 0001 textured ZrB₂ films deposited on Si(100) without external heating and at process conditions reported in [11], as well as bulk samples of polycrystalline ZrB₂. All films were deposited to a thickness of ~400 nm.

X-ray diffraction (XRD) $\theta/2\theta$ scans were performed to determine the structural properties of the films, using a Philips PW1820 diffractometer equipped with a Cu K α source operated at 40 kV and 40 mA. Figure 1 shows $\theta/2\theta$ diffractograms obtained from ZrB₂ films deposited at high temperature on 4H-SiC(0001) and Si(100) substrates. The film deposited on SiC(0001) (Figure 1a) shows peaks of high intensities corresponding to the 0001, 0002, 0003, and 0004 peaks of the ZrB₂ phase. Weaker ZrB₂ 10 $\bar{1}$ 1, 10 $\bar{1}$ 2, and 10 $\bar{1}$ 3 peaks can also be observed. Other peaks visible

are 000 $\bar{l}$ from the SiC substrate. The high intensities of the ZrB₂ 000 $\bar{l}$ peaks indicate that the film is well-ordered [12]. Recently we have shown that the intensity of these extra peaks decreases when the deposition temperature increases from 500 to 900 °C [4].

Figure 1: $\theta/2\theta$ XRD diffractograms of coatings deposited on (a) 4H-SiC(0001) at 900 °C, and (b) Si(100) at 850 °C.

The $\theta/2\theta$ diffractogram recorded from a film deposited on Si(100) (Figure 1b) displays a dominating Si(400) peak from the substrate and with the 10 $\bar{1}0$ peak being of highest intensity for ZrB₂, as well as weaker 000 $\bar{l}$, 10 $\bar{1}l$, 30 $\bar{3}0$ and 20 $\bar{2}3$ peaks. Faint 11 $\bar{2}0$ and 20 $\bar{2}1$ peaks are also detected. The intensity distribution among the ZrB₂ peaks shows that the film is weakly 10 $\bar{1}0$ textured and where their low intensities compared to that of the Si 400 peak is characteristic of a lower crystal quality compared to that of the film grown on SiC(0001).

The hardness (H) and reduced Young's modulus (E_r) as well as the elastic recovery (W_e) were investigated using a Hysitron Triboindenter TI950 instrument provided with a xSol™ high temperature heating stage operating in the range 25-600 °C. The nanoindentations were conducted using a high-temperature Berkovich diamond probe (Hysitron). An inert gas environment (N₂ containing 5% H₂) was used at an oven-like, gas flooded volume around the sample to prevent oxide formation. The specimen was first heated to a selected temperature. A waiting period of 10-20 min was used to reach thermal equilibrium. The indentation tip was then engaged in contact with the film surface, and 20-30 indents were performed. Once the experiments were finished, the temperature was increased to the next selected value. In all the nanoindentation

experiments the penetration depth of the indenter was kept lower than 10% of the film thickness to avoid influence from the substrate. H and E_r were calculated by the method of Oliver and Pharr using the unloading elastic part of the load–displacement curve [13]. The elastic recovery was calculated as $W_e = 100 \times (h_m - h_f) / h_m$, where h_m is the maximum penetration depth (produced at the maximum indentation load) and h_f corresponds to the final displacement after complete unloading. Tip-shape controls done after the tests at room temperature, 400 °C, and 600 °C have shown no change in the area function.

Table 1 gives H , E_r , and W_e measured at room temperature for different films. For comparison, the values for a ZrB_2 thin film deposited at room temperature, and a spark plasma sintered polycrystalline bulk sample obtained at 1900 °C [14] are also indicated. Thin film hardness decreases as the crystal quality of the films reduces but, interestingly, the elastic recovery measured at room temperature keeps at the same high value (96%) in all films. On the other hand, the ZrB_2 bulk sample has a $W_e = 81\%$.

Table 1: Comparison of hardness H , reduced elastic modulus E_r , and elastic recovery W_e measured at room temperature.

ZrB₂	H (GPa)	E_r (GPa)	W_e (%)
Epitaxial/SiC, deposited at 900 °C	47.3 ± 0.2	359 ± 8	96
Weakly textured/Si, deposited at 850 °C	30.8 ± 0.2	243 ± 8	96
0001 Textured/Si, deposited at ~25 °C	24.6 ± 0.4	291 ± 3	96
Spark-Plasma polycrystal sintered at 1900 °C (bulk)	31.1 ± 2.9	339 ± 13	81

Evidence about the high elasticity of the films was revealed by cross-sectional transmission electron microscopy (XTEM) imaging of indents. XTEM was prepared with the lift-out technique using a dual-beam focused ion beam scanning electron microscope (FIB-SEM 1540-ESB, Zeiss, Germany) with a Ga ion source. A Pt layer with 1 µm thickness was deposited prior to the milling to protect the indentation area. A FEI Tecnai G2-TF20-UT high resolution transmission electron microscope (HRTEM) with a field emission gun operated at 200 kV was used to observe the cross-sections images and corresponding selected area electron diffraction (SAED) patterns. A bright-field XTEM image of a 0001 textured ZrB_2 thin film deposited on Si(100) after being indented at room temperature with a load of 1.5 mN is displayed in figure 2d. No delamination was observed in the film/substrate interface, suggesting good interfacial bonding. The XTEM micrograph shows no indication of deformation or defects in the

nanoindentation zone: it seems that the films just elastically bounced back. Comparison of SAED patterns taken on the Berkovich indentation-deformed zone, as well at the left and right non-indented zones (figures 2a-c), indicate no crystalline degradation in the microstructure of the indented area. Furthermore, the micrograph reveals the presence of a pyramidal-shape transformed area on the silicon substrate than can be attributed to the nanoindentation. Dislocation activity phenomena and other defects can be observed in HRTEM (figure 2e), and the material around the indent seems to be highly stressed probably as a result of a phase transformation, leading to notable bend contour contrast, similar to previous studies for Berkovich nanoindentations on uncoated silicon [15]. Thus, the former observation of no phase transformation in the film supports the measured high elastic recovery of 96%, while the latter observation about the substrate damage shows that the film is stable in high stress fields.

Figure 2: SAED patterns obtained from a) left, b) middle, and c) right parts of indented ZrB_2 film imaged in d) and e) by XTEM and HRTEM (Si substrate only), respectively.

Figure 3 shows the hardness and reduced elastic modulus of the films deposited at 850 °C and 900 °C as a function of temperature. The epitaxial films deposited on 4H-SiC(0001) present, in the temperature range 25-350 °C, a hardness decrease from

47.3 $\pm$ 0.2 GPa to 34.9 $\pm$ 5.0 GPa, while E_r does not change significantly. For the temperature measurement range 400-600 °C, both H and E_r show a change of behavior: H increases up to 45.4 $\pm$ 9.5 GPa at 450 °C and then decreases to 32.8 $\pm$ 7.0 GPa at 600 °C. On the other hand, E_r show erratic changes in the range 338-389 GPa, to finish with a value of 369 $\pm$ 36 GPa at 600 °C, similar to the room temperature value. These observed changes starting at 350-400 °C are in agreement with a report by Xuan *et al* on single crystal ZrB₂ [6]. They correlated a change of hardness behavior at ~400 °C with an increase from single to multiple slip plane systems. For instance, NaCl and MgO have only {110} as slip plane system under indentation at room temperature, but multiple slip plane systems ({110}, {001}, and {111}) at higher temperatures [6]. Nakano *et al* has also reported that high temperature hardness indentation of single-crystal ZrB₂ depends on the indentation plane and the indentation direction, which activate different slip systems [5]. For the weakly 10 $\bar{1}0$ textured film (figure 3b), we measured a hardness decrease from 30.8 $\pm$ 0.2 GPa to 24.2 $\pm$ 7.1 GPa at 600 °C, while E_r slightly increases from 243 $\pm$ 8 to 255 $\pm$ 11 GPa. The increase of hardness and elastic modulus at temperatures above 500 °C for both samples (figures 3a and 3b) could be related to oxidation of the films or substrates. Rebelo *et al* [16] pointed out that during high-temperature nanoindentation of Al₂O₃ coatings in an Ar+N₂+H atmosphere (similar to our experiments), oxidation of their cemented carbide substrate might result in falsification of the load/unloading curves. IN our films, we have also seen indications for oxidation, e.g., interference colors at the sample surface after measuring up to 600 °C, which could also result in an apparent increase of H and E_r .

Figure 3: Hardness and reduced elastic modulus of ZrB₂ films (a) epitaxial film grown on 4H-SiC (0001) at 900 °C; (b) weakly textured film deposited on Si(100) at 850 °C, as a

function of temperature measurement. Error bars represent the mean value and statistical dispersion of 20-30 measurements per temperature.

The high temperature mechanical properties of our films are related to their crystal quality. To obtain films with the highest hardness and elastic modulus, the ZrB₂ films need to be epitaxially grown on SiC(0001) at 900 °C. Degraded mechanical properties are obtained, instead, when the ZrB₂ films have a weak texture. A low quality ZrB₂ microstructure is obtained as the result of a film/substrate reaction during growth on Si(100) at 850 °C. XTEM and HRTEM analysis of the film-substrate interface in this film reveals a fibrous ZrB₂ microstructure, a rough substrate surface, and the presence of an amorphous material on the interface (Figure 4).

Figure 4: XTEM micrograph of ZrB₂ film grown on Si(100) at 850 °C. The inset shows a HRTEM image of the Si/film interface

The few available high temperature hardness studies of bulk ZrB₂ that we discussed have employed Knoop [6] or Vickers [7-9] hardness measurements, making comparisons with our nanoindentation data on thin films difficult. Table 2 compares the H values at room temperature and 600 °C for our films and those from the

aforementioned published reports, as well as the relative variation of hardness in that temperature range. We can see that our films grown on 4H-SiC(0001) have the highest values at both temperatures, which can be correlated to the high crystal quality of our films, as we already observed in our epitaxial ZrB₂ films grown on Al₂O₃(0001) [12]. Regarding the film grown on Si(100) at 850 °C, the hardness values at both temperatures are slightly higher than the bulk single-crystal material reported by Nakano *et al* [5], and have lower hardness variation. Furthermore, the relative elastic modulus decrease $\Delta E/E$ in the temperature range of 25-600 °C, which can be correlated to atomic bonding deterioration, was reported to be ~3% [9,10], which is similar to the E_r reduction in our epitaxial and weakly textured samples grown on SiC(0001) and Si(100), respectively.

Table 2: Hardness temperature variation for different samples

ZrB ₂	H (GPa)		$\Delta H/H$ (%)
	25 °C	600 °C	
Epitaxial film/4H-SiC(0001)	47.3 ± 0.2	32.8 ± 7.0	30.6
Weakly textured film/Si(100)	30.8 ± 0.2	24.2 ± 7.1	21.4
Bulk single-crystal {0001} [5] (*)	27.0	15.0	44.4
Bulk single-crystal {10 $\bar{1}$ 0} [5] (*)	20.0	10.0	50.0
Bulk single-crystal [6] (*)	21.3	10.0	53.1
Bulk polycrystalline [7] (*)	30.0	8.5	71.7

(*) Published data does not provide error bars.

In summary, the hardness and relative elastic modulus of stoichiometric epitaxial ZrB₂ films were measured for the first time by a nanoindentation technique with *in situ* heating in the range 25-600 °C. The epitaxial film deposited on 4H-SiC(0001) have $H = 47.3 \pm 0.2$ GPa and $E_r = 359 \pm 8$ GPa at room temperature, and $H = 32.8 \pm 7.0$ GPa and $E_r = 369 \pm 36$ GPa at 600 °C. The 10 $\bar{1}$ 0 textured film on Si(100) have $H = 30.8 \pm 0.2$ GPa and $E_r = 243 \pm 8$ GPa at room temperature, which change to $H = 24.2 \pm 7.1$ GPa and $E_r = 255 \pm 11$ GPa at 600 °C. Nanoindentation, TEM, and SAED analyses reveals high elastic recovery of 96% for both films, with no phase transformations taking place during or after the indentations. Due to the superior hardness and elastic modulus at high temperature, ZrB₂ films are a promising material for applications which require hard films at high temperature, such as metal cutting.

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